

## Field of the Invention

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## Background of the Invention

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electrode layers. Flow field plates for directing the reactants across one surface of each electrode substrate are typically disposed on each side of the MEA.

5        A measure of electrochemical fuel cell performance is the voltage output from the cell for a given current density. Higher performance is associated with a higher voltage output for a given current density or higher current density for a  
10       given voltage output.

         A direct methanol fuel cell (DMFC) is a type of fuel cell in which methanol is directly oxidized at the anode. Although it may be operated on aqueous methanol vapour, a DMFC generally operates  
15       in a liquid feed mode on an aqueous methanol fuel solution. One problem which has been encountered with direct methanol fuel cells is performance degradation, that is, decrease in cell output voltage over time at a given current.

20       Hamnett et al. (Hamnett, A., Weeks, S.A., Kennedy, B.J, Troughton, G., Christensen, P.A., "Long-Term Poisoning of Methanol Anodes", Ber. Bunsenges. Phys. Chem. 94, 1014-1020 (1990)) conducted a study of long-term poisoning of  
25       methanol anodes. The work was carried out on half cells and not complete fuel cells. Platinum anodes and platinum-ruthenium anodes with a 2.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte and a reference electrode (mercury/mercurous sulphate) were employed.

With respect to pure platinum particle anodes, Hamnett et al. propose that poisoning on the electrode occurs by formation of a place-exchanged oxide which inhibits methanol adsorption.

5 This oxide formation occurs at high anode potentials and can be removed at lower potentials, that is, open circuit. On the other hand, Hamnett et al. show that the amount of oxidised platinum when using a platinum-ruthenium anode is  
10 substantially greater than in the pure platinum anode. They further find that the amount of oxidised platinum decreases after extended polarisation and that it appears that the deactivation of platinum-ruthenium anodes is  
15 related to a gradual decrease in the amount of oxides on the platinum surface. They conclude that platinum-ruthenium anodes are poisoned by a different mechanism and expect that periodic open-circuiting of the platinum-ruthenium anode would  
20 not be so effective in enhancing the lifetime as for platinum anodes and they show test results demonstrating this.

In another study Zelenay et al. (Zelenay, Piotr; Thomas, S.C., Gottesfeld, Shimshon, "Direct  
25 Methanol Fuel Cells: Recent Progress In Fuel Efficiency, Cell Performance And Performance Stability", Electrochemical Society Proceedings, Volume 98-27, 300-315) referring to active DMFC platinum-ruthenium anodes that can be operated for  
30 prolonged periods of time without noticeable loss

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osmium, platinum-iridium, as well as certain ternary mixtures.

The output power of the fuel cell may be reduced by reducing the current from the fuel cell at predetermined time intervals. The circuit may be switchable between a closed circuit condition in which the flow of electric current is permitted and an open circuit condition in which the flow of electric current is interrupted, reducing the output power of the fuel cell being effected by switching the current to the open circuit condition at predetermined time intervals.

The step of reducing the electric current in the circuit at predetermined time intervals may comprise the steps of operating the cell to provide electric current in the circuit for an operating period of about 0.5 to 4 hours; opening the circuit to terminate the flow of electric current for a rest period of about 1 second to 30 minutes; and ramping the current to increase from zero to a working value for a ramping period of up to 5 minutes.

The method may further comprise the step of interrupting the supply of fuel to the anode or the supply of oxidant to the cathode or both during the reduction of the output power of the fuel cell.

A direct feed solid polymer electrolyte fuel cell comprises an anode having a CO-tolerant catalyst and a cathode; a fuel supply line for directing fuel to the anode for the oxidation of

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### Brief Description of the Drawings

Figure 1a is a diagrammatic illustration of a solid polymer electrolyte fuel cell connected to a load in an external circuit;

Figure 1b is a diagrammatic illustration of a plurality of fuel cell stacks in series connected to a load in an external circuit;

Figure 2 is a plot of fuel cell voltage  
10 versus operation time, which illustrates  
periodically reducing the output power of the fuel  
cell;

Figure 3 shows polarization plots which illustrate the cathode mass transport degradation of a DMFC (single cell) operated continuously for a period of time;

Figure 4 shows polarization plots for a cell similar to Figure 3 but with the cell being operated with periodic load interruptions;

20            Figures 5a and 5b show AC impedance spectra  
of DMFCs that illustrate the effect of periodic  
load interruptions on cathode mass transport  
degradation;

Figures 5c and 5d show the AC impedance of  
25 the anodes for the same two DMFCs of Figures 5a and  
5b;

Figure 6 is a plot showing a direct comparison of cell voltage versus operation time for a DMFC operated using a 30 minute/30 second

recovery cycle technique and a similar DMFC operated continuously under load; and

Figure 7 is a plot of stack voltage versus operating time of a ten cell direct methanol fuel cell stack operated using two different recovery procedures.

#### Detailed Description of Preferred Embodiment(s)

In Figure 1a, reference numeral 10 generally indicates a direct methanol fuel cell comprising an anode 12 and a cathode 14 separated by a polymer electrolyte membrane 16.

The cell 10 has inlets 18 and 20 for directing fuel and oxidant to the anode 12 and cathode 14, respectively, as well as fuel and oxidant outlets 19 and 21.

Anode 12 and cathode 14 are connected by an external circuit 22 to an electrical load 24. A storage device or charge storage means, such as capacitor 26 is connected in parallel with the load 24. In place of capacitor 26 other suitable devices that act as buffers such, as a storage battery or the like, may be employed. The external circuit 22 is further provided with a switch 28 for opening and closing circuit 22 to the flow of electric power to load 24. When switch 28 is closed, cell 10 also charges the capacitor 26. When switch 28 is open, fuel cell 10 is disconnected from the load 24. During this time



capacitor 26 provides power to load 24 for a limited period of time.

A resistor 29 is connected in parallel to fuel cell 10. The resistor 29, which may be variable, is optionally provided and draws a limited amount of power from fuel cell 10. For instance, resistor 29 may simply represent the power draw by a peripheral subsystem associated with fuel cell 10 such as a fan or pump.

During normal operation, load 24 itself may be varied and the power output from fuel cell 10 would be varied accordingly between a normal operating minimum and maximum output (for example, in an automobile, the power output would vary between that required at idle and that required under full acceleration). Typically, the ratio of the maximum power output to that of the minimum power output (or "turndown ratio") for such a fuel cell system is less than about 60. In Figure 1a, the power consumed by resistor 29 is less than the normal operating minimum power output from fuel cell 10.

A variable resistor 31 is also provided in circuit 22. Variable resistor 31 may be operated when switch 28 is in the closed position in order to ramp the current up to a working value following an interruption period. Variable resistor 31 can also be used to prevent cell 10 from instantaneously shorting at the moment switch 28 is closed. Alternatively, variable resistor 31 may be

employed instead of switch 28 to reduce the current flow and therefore the output power of the cell 10 to less than the normal minimum power output of cell 10. The switch 28 and resistor 31 can of course be combined in one unit, for example, a variable resistor which can shut off current flow completely or simply reduce the current flow as described above. The value of variable resistor 31 is such that its power consumption is negligible when compared to that of load 24.

In the present example the fuel is an aqueous mixture of methanol that is supplied to the anode 12 in either liquid or vapour form and the oxidant is oxygen gas or compressed air.

The anode 12 comprises a CO-tolerant catalyst, such as a platinum-ruthenium (Pt-Ru) alloy. In the present example the anode comprises a porous carbon layer coated with the catalyst.

During normal operation of the cell 10, methanol is oxidized at the anode. The oxidation products are  $\text{CO}_2$ ,  $\text{H}^+$  and electrons, although there are some intermediates or by-products which may be present, such as carbon monoxide (CO), formaldehyde (HCHO), formic acid (HCOOH), methyl formate ( $\text{HCOOCH}_3$ ) and dimethoxymethane ( $\text{H}_2\text{C}(\text{OCH}_3)_2$ ), depending upon the operating conditions.

At the cathode, water is produced. In addition water accumulates at the cathode due to electro-osmotic drag and diffusion from the anode. Depending on the membrane, some methanol may cross

over to the cathode where it is oxidized. This results in methanol and its oxidation products being present at the cathode.

5 The fuel cell 10 is operated at constant or  
varying power, as required, with interruptions of  
the power at predetermined time intervals. These  
interruptions may occur irregularly but periodic  
interruptions may be preferred. This procedure is  
10 effected in three stages or steps as illustrated in  
Figure 2. During stage one, switch 28 is closed  
and cell 10 provides power to load 24, while also  
charging capacitor 26. The duration of this stage  
is preferably greater than 30 minutes.

15 During stage two, switch 28 is open so that  
external circuit 22 is open, that is, the cell is  
not providing load 24 with electrical power. The  
duration of this stage is preferably less than 30  
seconds.

20 During stage three, switch 28 is closed so  
that electric current again flows in circuit 22.  
However the current does not have to be  
instantaneously returned to the value immediately  
prior to opening of switch 28, but can be ramped up  
to this value, either in stepwise fashion or  
25 linearly, for example, by means of variable  
resistor 31 in series with switch 28 or other  
means. The duration of stage three is about 2  
minutes. In this way, the cell is subjected to  
periodic load interruptions, that is, periodic open

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circuit periods during which the flow of current in the circuit is interrupted.

It has been found that the above procedure has the effect of counteracting performance degradation of the cell 10. The procedure may be carried out manually or automatically, for example, by means of suitable software with the use of a computer. When the cell 10 is held at open circuit, or if the current flow in the circuit 22 is reduced below the normal operating minimum output, the normal reactions of methanol oxidation at the anode and oxygen reduction at the cathode no longer occur or the progress of these reactions is reduced. Without being bound by theory, the enhancement of cell performance is presumed to occur as a result of improvement of cathode mass transport properties, that is, improvement of transport of oxidant to the cathode catalyst that may arise from removal of reaction product (water) from the cathode. Therefore, this operating procedure works to improve long-term performance of the cell 10 by recovering the reversible performance degradation of the cell 10 when held at open or almost open circuit. Possible processes occurring which may lead to recovery include improved water removal at the cathode, improved carbon dioxide and intermediates removal at the anode, and improved removal of crossover methanol oxidation products at the cathode. In addition, the frequent repetition of the recovery technique

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electricity to the load 40. For example, if stack 30 is to be held at open circuit then switches 1a, 2, and 3 will be closed while switches 1, 2a, 3a and 4a will be open. If stack 34 is to be held at open circuit then switches 1, 2 and 3a will be closed, while switches 1a, 2a, 3 and 4a will be open. In this manner the current by-passes the chosen stack and the stack remains at open circuit until the switches are changed to allow current to flow through the stack.

With this type of configuration, each of the stacks can be operational and individual stacks can be held at open circuit when desired, while the remainder of the stacks still provide power.

### Examples

Polarization plots (voltage versus current densities) are shown in Figure 3 and illustrate the cathode mass transport degradation of a DMFC (single cell A) operated continuously at  $200 \text{ mA/cm}^2$  for 16 hours. Plots A1(O<sub>2</sub>) and A1(air) show the initial polarization results for the DMFC when operated on pure oxygen or air oxidant respectively. The effect that diluting the oxidant stream with about 80% inert gas (nitrogen) has on initial performance is indicated by the difference between plots A1(O<sub>2</sub>) and A1(air). Plots A2(O<sub>2</sub>) and A2(air) show the polarization results for the same cell on pure oxygen and air respectively after only

16 hours of continuous operation. The difference between the air and pure oxygen polarization plots after continuous operation has become more substantial, particularly at higher current densities (that is, the difference  $A2(\text{air}) - A2(\text{O}_2)$  is greater than the difference  $A1(\text{air}) - A1(\text{O}_2)$ , particularly at higher current densities). In comparison, Figure 4 shows polarization results for a similar DMFC (cell B) that had been operated for 1978 hours with periodic load interruptions wherein the cell was open circuited every 30 minutes for a period of 30 seconds and then the load was ramped up to normal over a period of 2 minutes (a "30 minute/30 second recovery cycle"). Plots  $B1(\text{O}_2)$  and  $B1(\text{air})$  show the initial performance on pure oxygen and air respectively and plots  $B2(\text{O}_2)$  and  $B2(\text{air})$  show the performance after 1978 hours of operation on pure oxygen and air respectively. The difference between the air and pure oxygen polarization plots has not changed substantially after prolonged operation (that is, the difference  $B2(\text{air}) - B2(\text{O}_2)$  is about the same as the difference  $B1(\text{air}) - B1(\text{O}_2)$  even after prolonged operation). The load interruption method allowed the cell to operate over 120 times longer with less performance degradation.

Figures 5a-d show AC impedance spectra of the electrodes in certain tested DMFCs. In obtaining these spectra, first a spectrum is taken of the complete DMFC operating under normal conditions

(that is, oxidant and fuel are supplied to the cathode and anode respectively) which gives the spectrum of the combined impedances of cathode, electrolyte, and anode. Then, a spectrum is  
5 obtained under similar conditions but with nitrogen gas supplied to the cathode, thus essentially making the cathode a reference electrode. The spectrum obtained in this case is then that of the combined impedances of electrolyte and anode. The  
10 spectrum of the cathode is then derived by taking the difference between the two spectra.

Figures 5a and 5b are AC impedance spectra of DMFCs that are also illustrative of the effect that the inventive method has on cathode mass transport  
15 degradation. The spectra were taken at  $250 \text{ mA/cm}^2$  over a frequency range from 65 KHz to 0.21 Hz. Figure 5a shows the AC impedance spectra for the cathode electrode of a DMFC (cell C) similar to those of Figures 3 and 4. The DMFC of Figure 5a  
20 however had been operated for 1090 hours and an attempt was made to improve performance via a different anode starvation recovery procedure every 24 hours (involving starving the anode of fuel which causes a temporary change in anode  
25 potential). Plot C1 shows the initial cathode impedance spectrum and plot C2 shows the spectrum after 1090 hours of operation. The cathode impedance has increased substantially. On the other hand, Figure 5b shows the cathode impedance  
30 spectra for the aforementioned DMFC (cell B) of



Figure 4. Plot B1 shows the initial cathode impedance spectrum and plot B2 shows the spectrum after 1978 hours of operation. There is no significant increase in cathode impedance.

5        Figure 5c and 5d are also presented to show the AC impedance of the anodes plus electrolytes for the same two DMFCs. In this case, the spectra were taken at 50 mA/cm<sup>2</sup>. Figure 5c shows the AC impedance of the anode plus electrolyte of cell C  
10 initially (plot C1) and after 1090 hours of operation (plot C2). Figure 5d shows the AC impedance spectrum of the anode plus electrolyte of cell B initially (plot B1) and after 1978 hours of operation (plot B2). There is no significant  
15 difference in the anode plus electrolyte impedances before and after prolonged operation in either cell. The predominant loss in performance thus appears to originate from effects at the cathode.

Table 1 shows the degradation rate of cell  
20 voltage for the DMFC of Figure 4 when subjected to various combinations of load application time, open circuit time, and ramp time (that is, stage 1, stage 2, and stage 3 times). Each combination gave a lower degradation rate than that for continuous  
25 operation under load (1500  $\mu$ V/hr as determined from operating continuously for 16 hours).

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Table 1

Load On Steady (min) Stage 1	Open Circuit(s) Stage 2	Load On Ramp(s) Stage 3	Degradation Rate ( $\mu\text{V/hr}$ )
27.5	30	120	26
27.5	3	120	6
237.5	30	120	50
29	30	30	0-70
27.5	30*	120	200-400
27.5	1	120	120
29.3	30	10	2
29.3	1	10	220
29	3	30	80
1440	30	120	170**

5   \*   Cell was not open circuit but was operated at a reduced current density of  $50 \text{ mA/cm}^2$ .

    \*\*    $420 \mu\text{V/hr}$  over the first 1440 minute load on period.

10       Figure 6 shows a direct comparison of cell voltage versus operation time for a DMFC operated using the "30 minute/30 second recovery cycle" technique and a similar DMFC operated continuously under load. Plot C shows the voltage of the

15   conventional DMFC which degraded at a rate of about  $300 \mu\text{V/hr}$ . Plot I shows the voltage of the DMFC operated using the "30 minute/30 second recovery cycle" technique. After 1000 hours of testing,

this DMFC showed a degradation rate of only about 26  $\mu\text{V/hr}$ .

In addition to interrupting the current, the supply of fuel or oxidant or both fuel and oxidant to the anode and cathode, respectively may be interrupted. This system interruption should be timed to occur simultaneously with the current interruption stage two, described above.

A direct methanol compact power stack comprising 10 fuel cells was then tested using two different recovery procedures. Over about the first 1200 hours of operation, the stack was switched to an open circuit condition every 24 hours for about 30 minutes. (On occasion, the stack stayed under load for more than 24 hours between open circuits). In addition, the flow of fuel and oxidant were also interrupted during these open circuit periods. Thereafter, periodic switching to an open circuit condition with reactant interruption continued using the "30 minute/30 second recovery cycle" procedure. Figure 7 shows the stack voltage of this stack versus operating time. Overall, a markedly improved 15  $\mu\text{V/hr}$  per cell degradation rate was observed for over 1700 hours of operation at 200  $\text{mA/cm}^2$ .

While particular elements, embodiments and applications of the present invention have been shown and described, it will be understood, of course, that the invention is not limited thereto

since modifications may be made by those skilled in the art without departing from the scope of the present disclosure, particularly in light of the foregoing teachings.

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